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# Crosslinked polyimide foams derived from pyromellitic dianhydride and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,3-trifluoroethane with poly(α-methylstyrene)

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A new route for the synthesis of high glass transition temperature, thermally stable polymer foams with pore sizes in the nanometre regime has been developed, using compositionally asymmetric microphase-separated block copolymers where the minor component (poly(α-methylstyrene)) is thermally labile and the major component (polyimide) is thermally stable. The minor component can unzip to its monomer upon heating, and the decomposition products can diffuse out of the film, leaving behind pores embedded in a matrix of the thermally stable component. In this study, the polyimide block was crosslinked with ethynyl functionalities to obtain a stable porous structure. The decomposition of the α-methylstyrene in the block copolymer was studied by thermogravimetric, dynamic mechanical and thermomechanical analyses. Mild conditions were required to avoid rapid depolymerization of the α-methylstyrene and plasticization of the polyimide matrix. The foams showed pore sizes with diameters up to a micrometre in size as well as the expected reduction in the mass density. However, the crosslinking of the matrix as a means of stabilizing the expected nanofoams was not successful.

**(Keywords: polyimide foams; crosslinking; block copolymer)**

## *Introduction*

A new approach to lower dielectric constant, high performance polymers has been developed. This approach involves the generation of a foam or porous structure where the reduction in dielectric constant is achieved by replacing the polymer with air, which has a dielectric constant of 1. However, for thin film microelectronic applications, it is critical that the pore size be much smaller than the film thickness and any microelectronic features if the reduction in dielectric constant is to be of use. A method has been developed for generating a high temperature polymer foam which leads to pore sizes in the nanometre regime. Foams can be prepared from microphase-separated compositionally asymmetric block copolymers comprised of a thermally stable and a thermally labile material, where the latter is the dispersed phase[1–4]. Upon heating, the thermally unstable block undergoes thermolysis leaving pores the size and shape of which are commensurate with the initial copolymer morphology. Triblock and graft copolymers comprising polyimide with either poly(propylene oxide)[1–3], poly(α-methylstyrene)[4] or poly(methyl methacrylate)[2] as the thermally labile components have been shown to produce nanofoams. For the poly(propylene oxide) and poly(methy methacrylate) based copolymers, the porosity of the polyimide nanofoams was considerably less than the volume fraction of the thermally labile block[1–3]. The inefficiency in the foaming process was attributed to a combination of both surface effects and partial plasticization of the high temperature polymer matrix from the degradation products. Markedly different behaviour was observed for the poly(α-methylstyrene) based copolymers, where the pore size and porosity were significantly larger than expected from the copolymer morphology and the volume fraction of α-methylstyrene[4]. The degradation product was found to both plasticize the matrix and act as a 'blowing agent'. To minimize the interaction of the degradation products with the polyimide matrix, thermosetting reactions were employed. In this paper the synthesis and characterization of such block copolymers are described.

## *Experimental*

*Materials.* *N*-Methyl-2-pyrrolidone (NMP; Aldrich) was used without further purification, and pyromellitic dianhydride (PMDA; Chriskev Co.) was sublimed three times prior to use. The aminophenyl carbonate terminated poly(α-methylstyrene) oligomers were prepared according to a literature procedure[4]. The diethyl pyromellitate diacyl chloride was prepared as described by Volksen *et al.*[5]. The 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA) was prepared according to literature procedures[6,7]. The 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane (3FET) was prepared according to a literature procedure[8].

*Polymerizations.* The amic ester–α-methylstyrene triblock copolymers were prepared by the co-reaction of the amino-terminated α-methylstyrene oligomers with 3FDA, 3FET and PMDA diethyl ester diacyl chloride in NMP in the presence of *N*-methylmorpholine. A

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**Table 1** Characteristics of imide–α-methylstyrene copolymers containing ethynyl functionalities

| Sample entry | Ethynyl composition (wt%) | α-Methylstyrene composition |  | Content of α-methylstyrene (vol%) | Porosity (%) |
|---|---|---|---|---|---|
|  |  | Charge | Incorporated |  |  |
| Copolymer 1 | 25 | 25 | 24 | 27 | 46 |
| Copolymer 2 | 40 | 25 | 26 | 30 | 56 |

detailed procedure designed to prepare an amic ester–α-methylstyrene copolymer (with α-methylstyrene content of 25 wt% and a 3FET content of 40%) using an α-methylstyrene oligomer of molecular weight 17 000 g mol$^{-1}$ is given in *Table 1* (copolymer 2). A three-necked flask equipped with an overhead stirrer and addition funnel was charged with α-methylstyrene oligomer (0.25 g, 0.000 007 3 mol), 3FDA (0.281 g, 0.000 82 mol) and 3FET (0.2005 g, 0.000 547 mol), and carefully rinsed in with 15 ml of NMP and 5 ml of tetrahydrofuran (THF). The solution was then cooled to −5°C and *N*-methylmorpholine (0.316 g, 0.003 124 mol) was added to the solution. The PMDA diethyl ester diacyl chloride (0.479 g, 0.001 41 mol) was dissolved in ~25 ml of methylene chloride and added in increments over a 2 h period so as to slowly approach the stoichiometric end point. The polymerization was allowed to proceed overnight. The polymer was isolated by precipitation in methanol/water, rinsed with water (to remove excess salts) and cyclohexane (to remove possible homopolymer contamination), and dried in a vacuum oven.

*Foam formation.* The copolymers were dissolved in NMP at a concentration of 9–15% solids. Coatings of 10–25 μm in thickness were obtained by doctor-blading onto larger glass substrates. The removal of the solvent and imidization, if required, were accomplished by heating the polymer films to 265°C at 5°C min$^{-1}$ and maintaining them at 265°C for 1.5 h in a nitrogen atmosphere. The films were then heated over a 4 h period to 325°C for 2 h to effect the decomposition of the α-methylstyrene block[4].

*Characterization.* Glass transition temperatures, $T_g$, were measured on a DuPont 1090 instrument at a heating rate of 10°C min$^{-1}$. A Polymer Laboratories Dynamic Mechanical Thermal Analyzer operated at 10 Hz with a heating rate of 10°C min$^{-1}$ in the tension mode was used to measure the dynamic mechanical properties. Isothermal and variable temperature (5°C heating rate) thermal gravimetric analysis (t.g.a.) measurements were performed on a Perkin–Elmer model TGA-7 in a nitrogen atmosphere. The density column was calibrated against a set of beads of known density at 25°C. Transmission electron microscopy (TEM) analysis was performed on a Phillips 12 520 Instrument at 100 kV. The samples for TEM were prepared by ultramicrotoming the films at room temperature. Fourier-transformed infra-red (*FT*i.r.) measurements were made on an IBM Instrument IR44 with an MCT detector.

### *Results and discussion*

The block copolymer approach to polyimide nanofoams requires the use of a thermally labile coblock which decomposes at a temperature which is sufficiently high to permit standard film preparation and solvent removal, yet well below the $T_g$ of the polyimide to avoid collapse of the foam. Poly(α-methylstyrene) decomposes at ~290°C and the $T_g$ of 3FDA/PMDA polyimide is approximately 440°C, thus an ample window for film and subsequent foam formation is realized. The major concern in generating a crosslinked, high $T_g$ nanofoam is whether efficient network formation could be achieved at temperatures below the decomposition of the labile block, since any thermosetting reaction would be diffusion limited in the glassy polyimide. To this end, the poly(amic alkyl ester) precursor to the polyimide was employed in the block copolymer approach to nanofoam formation. Prior to imidization, a $T_g$ or softening has been observed at ~120°C for poly(amic alkyl ester)s derived from 3FDA with the *meta* isomer of diethyl ester diacyl chloride of PMDA[9]. Thus, subsequent transformations are possible prior to the onset of imidization (~250°C) and well below the decomposition temperature of the α-methylstyrene coblock. The ethynyl functionality has been shown to crosslink thermally in the appropriate temperature regime (200–300°C) and the resulting networks give the requisite thermal stability[10]. Poly(amic alkyl ester)s have been prepared with several ethynyl compositions, and swelling measurements of the networks showed substantially less α-methylstyrene uptake with increasing ethynyl compositions than the corresponding non-crosslinked material (*Figure 1*). The minimized interaction of the α-methylstyrene with the crosslinked polyimide is anticipated to produce nanofoams with controlled pore size and minimal interconnectivity.

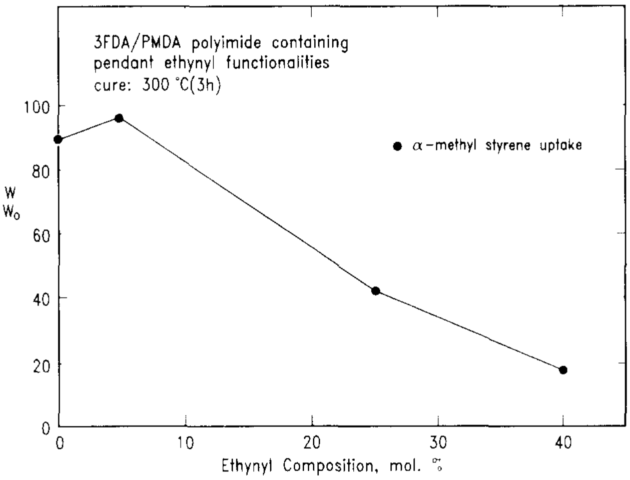
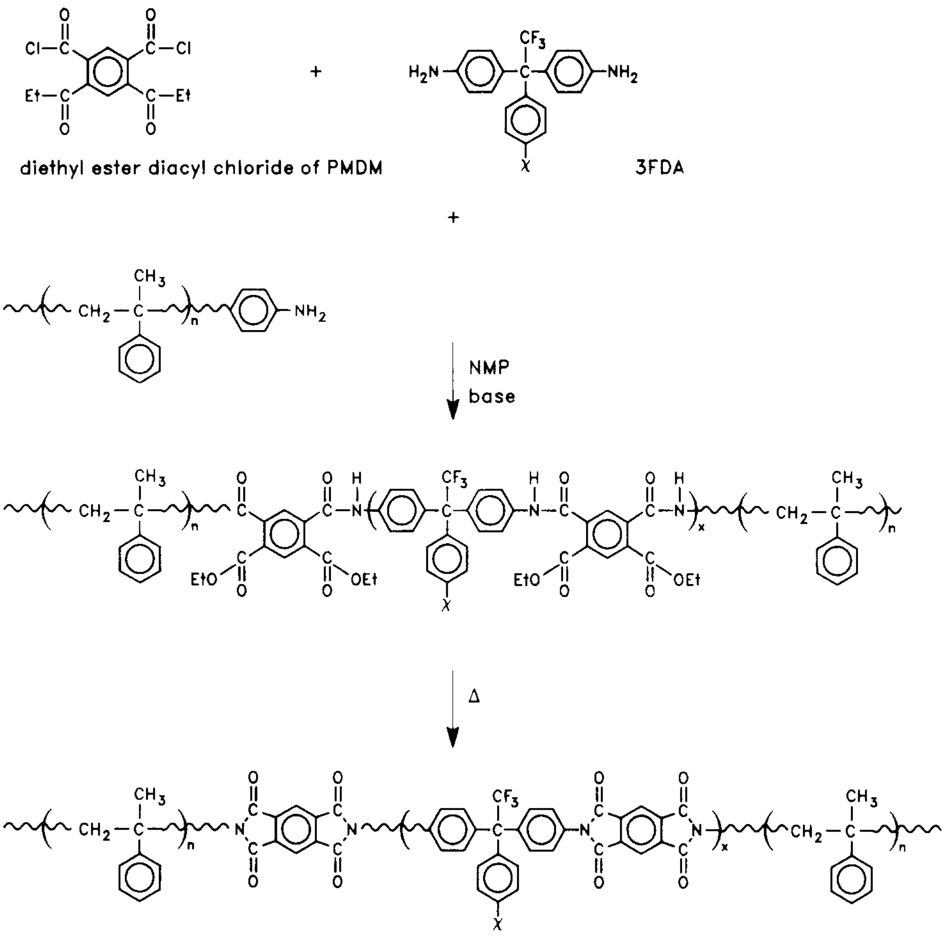


**Figure 1** The α-methylstyrene uptake for the crosslinked 3FDA/PMDA polyimide containing various compositions of ethynyl functionality

The poly(amic alkyl ester) precursor to polyimide copolymers also allows more synthetic flexibility than the poly(amic acid) analogue since it is soluble in a variety



| | X |
|---|---|
| Copolymer 1 | 75 mol%–H, 25 mol%–C≡CH |
| Copolymer 2 | 60 mol%–H, 40 mol%–C≡CH |

**Scheme 1**

of solvents and solvent mixtures. This allows copolymers with greater structural variety in the polyimide backbone, as well as in the coblock type, length and composition. The hydrolytically stable poly(amic alkyl ester) precursors may be isolated, characterized and washed to remove possible homopolymer contamination prior to imide formation. Furthermore, the poly(amic alkyl ester) route may favourably influence the morphology of the subsequent imide copolymers. Since imidization occurs at higher temperatures, there is sufficient mobility to allow a more complete microphase separation.

The synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride in methylene chloride to a solution of the α-methylstyrene oligomer, 3FET and 3FDA in an NMP/THF solvent mixture containing pyridine as the acid acceptor (*Scheme 1*). Although poly(α-methylstyrene) is soluble in NMP, the polymerization often becomes cloudy upon formation of the poly(amic alkyl ester). The addition of 15–25% THF produced clear solutions. The solids composition was maintained at approximately 15% for each polymerization. Completion or near-completion of the polymerization was taken at the point where the viscosity increased dramatically. The copolymers were isolated in a methanol/water mixture, rinsed with water to remove remaining salts, rinsed with cyclohexane to remove possible poly(α-methylstyrene) homopolymer and dried at 50°C (24 h) under vacuum.

Several imide–α-methylstyrene copolymers were prepared with several ethynyl compositions. The ethynyl compositions (i.e. the mol% of 3FET relative to 3FDA) were 25 and 40% (copolymers 1 and 2, respectively) (*Table 1*). Polyimides with ethynyl contents below these values showed minimal improvements in solvent resistance. The α-methylstyrene compositions were deliberately maintained low so as to obtain discrete, as opposed to interconnected, poly(α-methylstyrene) domains. The composition of α-methylstyrene in the copolymer was assessed by t.g.a., by measuring the weight retention after decomposition of the labile block. In each case, the composition of α-methylstyrene incorporated agreed closely with that charged (*Table 1*). The use of the monofunctional poly(α-methylstyrene) with the polyimide monomers produced an ABA triblock architecture, where the α-methylstyrene coblock comprised the A block. The average molecular weight of the α-methylstyrene block is identical to that of the preformed oligomers, while the molecular weight of the imide block is controlled by the stoichiometric imbalance between the dianhydride and diamine. Due to the high molecular weight of the α-methylstyrene, the imbalance is minimal and the molecular weight of the polyimide block should be high.

A key component in generating a nanofoam is the ability to process the block copolymer precursor by conventional methods. The α-methylstyrene decomposition temperature is high enough to allow removal of common solvents and effect the imidization and crosslinking reaction prior to void formation. The copolymers were dissolved in NMP, cast onto a substrate and cured to 265°C for 1.5 h to remove the solvent. Volksen *et al.*[5] found that the temperature range over which imidization occurred for the poly(amic ethyl ester) derived from PMDA/ODA was from 240 to 355°C with a maximum in the rate at 255°C. Likewise, the temperature range over which crosslinking occurs is between 200 and 300°C. Consequently, a cure schedule of 265°C for 1.5 h is believed to be sufficient to both crosslink and imidize, at least to a considerable extent, the copolymer. The dynamic mechanical results for the copolymers prepared in this manner are shown in *Figure 2*. Two transitions were observed in each case, indicative of microphase-separated morphologies. The transition occurring near 160°C is similar to that seen for the α-methylstyrene oligomer used in the synthesis. Furthermore, the transitions associated with the α-methylstyrene component are sharp, indicating that the phase boundaries are sharp. The transitions associated with the imide blocks are high (>440°C), and consistent with a crosslinked 3FDA/PMDA polyimide. In each case, however, a modulus increase can be observed at ~320°C consistent with the decomposition and evolution of the α-methylstyrene phase. The thermal mechanical analysis (t.m.a.) also confirmed the microphase-separated morphology of the copolymers (*Figure 3*). In these experiments, a small tensile deformation was applied during heating. The deformation is plotted as a function of temperature. As expected, the samples expanded with temperature up to ~155°C, and as the sample approached the $T_g$ of the α-methylstyrene component where an expansion was expected, a small contraction was observed. This contraction is believed to be associated with residual stress resulting from solvent evaporation and imidization. A rapid expansion in the sample then occurred up to ~280°C whereupon a small contraction was observed. This is consistent with the formation and simultaneous collapse, or at least partial collapse, of the cellular structure. The sample continues to expand up to ~350°C, where a precipitous contraction in the sample is observed. This can be attributed to a plasticization of the polyimide by the residual α-methylstyrene. It is noteworthy that this dual evolution of the α-methylstyrene was not observed in the linear polymer analogues.

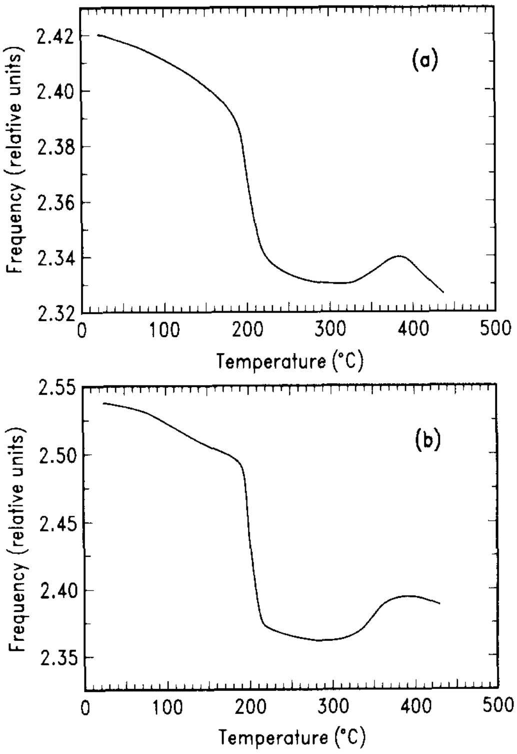


**Figure 2** Dynamic mechanical analysis for (a) copolymer 1 and (b) copolymer 2

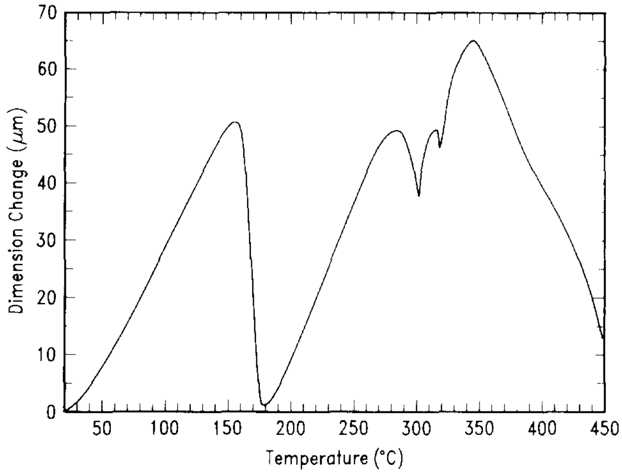


**Figure 3** Thermal mechanical analysis of copolymer 2

The generation of the nanofoam was accomplished by decomposition of the α-methylstyrene block. From the previous discussion, minimal decomposition temperatures must be employed to avoid plasticization and collapse of the foam structure. The optimum cure schedule was found to be 265°C for 1.5 h followed by a slow heating to 325°C over a 4 h period and holding at temperature (325°C) for 2 h. The samples, once cured to 265°C for 1.5 h, were transparent, consistent with a microphase-separated morphology. However, once foamed, the samples became opaque which suggested that the pore size was not commensurate with the initial block copolymer morphology. The porosity, as measured by i.r., for copolymers 1 and 2 was 46 and 56%, respectively[10]. These values are considerably higher than the volume fraction of α-methylstyrene in the copolymer. Furthermore, this value is considerably higher than that observed for the linear polymer analogue previously reported.

The electron micrographs shown in *Figures 4* and *5* reveal a rather unusual morphology. Embedded in the polyimide matrix are clusters of pores with dimensions on the micrometre scale. Within these clusters are pores with dimensions on the scale of hundreds of nanometres. The origin of the opacity of the foamed materials clearly arises from the scattering of light from the large clusters of pores. Even if these clusters did not exist, the pores within the clusters are sufficiently large to produce opacity in the sample. Neither pore size is commensurate with the initial size of the poly(α-methylstyrene) microdomains in the copolymer, which are of the order of tens of nanometres. Consequently,

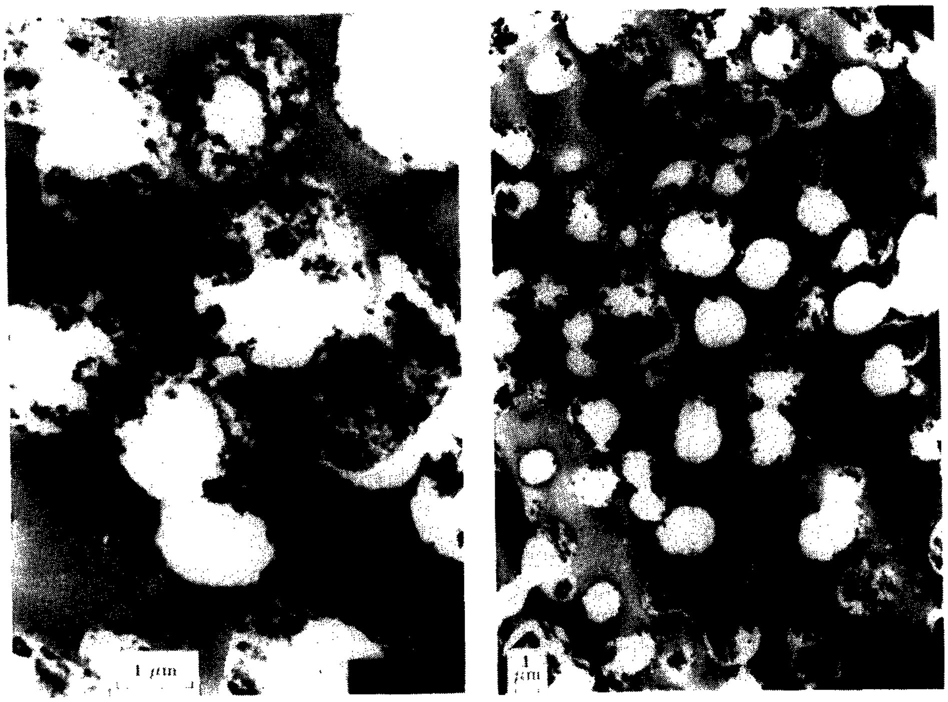


**Figure 4** TEM micrograph of foamed copolymer 1

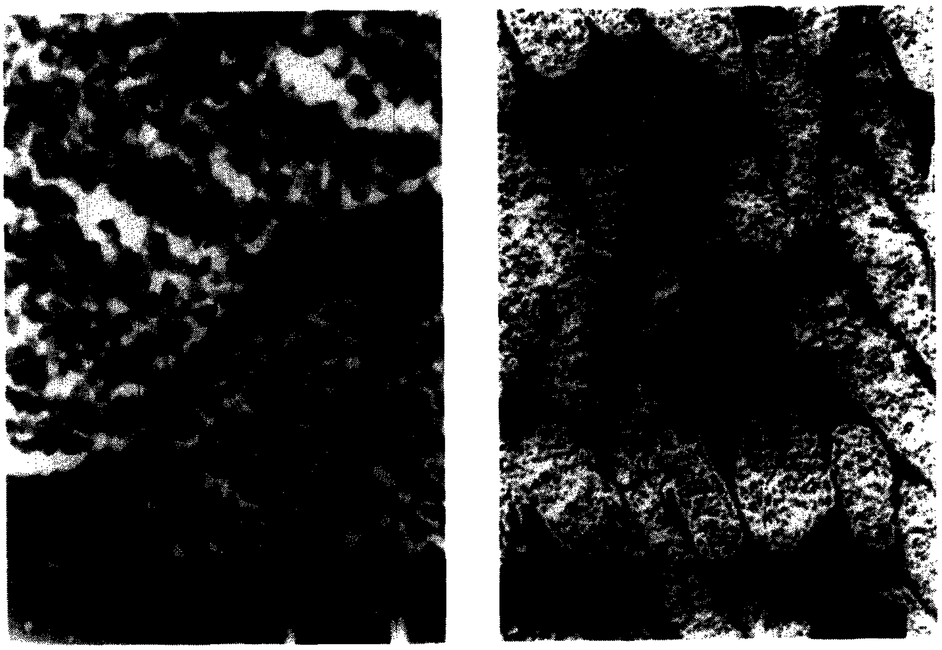


**Figure 5** TEM micrograph of foamed copolymer 2

the degradation of the poly($\alpha$-methylstyrene) block is sufficiently rapid and the matrix polyimide must be sufficiently plasticized to cause an effective blowing of the pores and, interestingly, the pore sizes are considerably larger than those observed for the linear analogue.

One of the surprising features of the micrographs is that the morphology is very inhomogeneous, with large areas of the matrix polyimide containing low concentrations of voids. This result can only be interpreted by a collapse of the foam structure. This, in fact, runs counter to the original intent of the crosslinking. The crosslinking was incorporated into the polyimide matrix to stabilize the foam structure by reducing the interaction between the polyimide and $\alpha$-methylstyrene to minimize plasticization. This, as can be seen, was not achieved. The origin of this lies in the rapidity at which the poly($\alpha$-methylstyrene) block decomposes. During the decomposition to monomer, the monomer plasticizes the matrix, thereby reducing the viscosity of the matrix and allowing the structure to collapse. During this decomposition, further crosslinking occurs. However, the rate at which the crosslinking occurs must be much slower than the decomposition of the poly($\alpha$-methylstyrene). The question still remains as to why a heterogeneous structure develops. One possible explanation for this is that the non-decomposed copolymer of the polyimide and poly($\alpha$-methylstyrene) acts as an emulsifying agent between the polyimide homopolymer and the $\alpha$-methylstyrene monomer generated during the decomposition. Surface tension would drive the system to maximize the size of the domains; however, the crosslinking that is occurring eventually freezes the system in a highly non-equilibrium state. In addition, the solubility of the $\alpha$-methylstyrene in the polyimide matrix will decrease with increasing degree of crosslinking (*Figure 1*). The reduced solubility or plasticization explains, to some extent, the dual or expanded evolution of the $\alpha$-methylstyrene degradation product observed by t.m.a. While this is speculative, it does provide a reasonable explanation for the unusual morphology seen in the micrographs.

## *Summary*

Microphase-separated block copolymers comprising a thermally stable polyimide as the matrix or dominant phase with a thermally unstable material have been prepared. In this study, the polyimide block was crosslinked with ethynyl functionalities to obtain a stable porous structure. The copolymers were designed in such a way as to permit conventional solvent processing techniques, i.e. spin-coating and doctor-blading, etc. The copolymers were prepared via a poly(amic alkyl ester) route, since this precursor has a $T_g$ of $\sim 100°C$ which provides the requisite mobility for the crosslinking reaction to occur. The $\alpha$-methylstyrene compositions were deliberately maintained low so as to produce discrete domains of the thermally labile component in a high temperature polymer matrix. Microphase-separated morphologies were observed by dynamic mechanical analysis. A processing window for the formation of a foam was established. TEM measurements showed that the sizes of the pores generated were large ($\sim 1$ $\mu$m). This discrepancy in the pore size was attributed to a plasticization of the polyimide matrix coupled with rapid volatilization of the poly($\alpha$-methylstyrene) which served as a blowing agent. Consequently, the crosslinking of the polyimide matrix was not sufficient to minimize the plasticization and subsequent blowing.

## *Acknowledgement*

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## *References*

1 Hedrick, J. L., Labadie, J. W., Russell, T. and Wakharker, V. *Polymer* 1993, **34**, 22
2 Hedrick, J. L., Russell, T. P., Lucas, M., Labadie, J. and Swanson, S. *Polymer* in press
3 Charlier, Y., Hedrick, J. L., Russell, T. P. and Volksen, W. *Polymer* in press
4 Charlier, Y., Hedrick, J. L., Russell, T. P. and Jerome, R. *Polymer* in press
5 Volksen, W., Yoon, D. Y. and Hedrick, J. L. *Mater. Res. Soc. Symp. Proc.* 1991, **23**, 227
6 Rogers, M. E., Mog, T. M., Kim, Y. S. and McGrath, J. E. *Mater. Plas. Soc. Symp.* 1992, **264**, 13
7 Rogers, M. E., Brink, M. H. and McGrath, J. E. *Polymer* 1993, **34**, 849
8 Jensen, B. J., Hegenrother, P. M. and Ninokogu, G. *Polymer* 1993, **34**, 639
9 Jayaraman, S., McGrath, J. E., Wilkes, G. and Hedrick, J. L. *Polymer* submitted
10 Sanchez, M., Hedrick, J. L. and Russell, T. P. *J. Polym. Sci., Polym. Phys. Edn* in press